Luminescence of Silver Bromoiodide Crystals*

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Crystals of simple and mixed silver halides are known to show a strong fluorescence but little afterglow at low temperatures. However, the slow buildup of luminescence under weak excitation indicates the presence of effective trapping processes. These processes have been studied in more detail on silver bromoiodide crystals. The lifetimes of the trapping states were estimated by observing the dependence of buildup rates on the dark interval between two exposures. The trapping states are also revealed by the effects of infrared radiation. If applied during excitation, it reduces the stationary brightness; if it is applied in the interval between exposures, it reduces the rate of re-excitation. The pattern of behavior of these phosphors is interpreted by a model of the type generally used in the description of zinc sulfide and similar photoconducting phosphors. If the absence of afterglow is taken into account, the model requires that the efficiency of the phosphor should increase with the square root of the exciting intensity. This has been confirmed experimentally over a range of 3 powers of 10. An afterglow can be produced in the silver bromoiodide by incorporating certain divalent cations (such as Cd^{++} or Sr^{++}) into the crystal. From an extension of the model to this more complex system, a number of emission and stimulation effects can be deduced which have been found in a series of qualitative observations.

1. INTRODUCTION

IT has been known for some time that silver halides of high purity show a strong fluorescence at low temperatures. Randall[1] observed fluorescence of pure silver chloride crystals, although he believed that residual impurities were probably responsible for the observed fluorescence. About the same time, Meidinger[2,3] observed low-temperature fluorescence of silver chloride, bromide, iodide, and bromoiodide (several percent iodide) emulsions. For the bromoiodide emulsions, Meidinger reported a bright green fluorescence at the temperature of liquid nitrogen, under excitation by blue or ultraviolet radiation. Farnell and Burton[4] have examined in some detail the low-temperature fluorescence of the silver halides. They reached the conclusion that, at sufficiently low temperatures, pure silver halide crystals show a strong fluorescence, but they found no visible afterglow or phosphorescence. For silver bromide-silver iodide mixed crystals, Farnell and Burton confirmed Meidinger's observations on the luminescence of emulsions. This luminescence shows no afterglow, and has been interpreted by Farnell and Burton as an edge luminescence, that is, as a resonance fluorescence which becomes observable at wavelengths near the absorption edge of the crystal.

We have more recently made a limited study of the luminescence of silver halide crystals, particularly of silver bromide-silver iodide mixed crystals, in which we investigated the buildup of emission under excitation, the effects of infrared radiation on the luminescence, and cation-activated fluorescence. These observations reveal a pattern of behavior which places the silver halides clearly in the class of photoconducting phosphors.[5] The simplest model for such a phosphor, with one type of electron trap and one type of hole trap, serves well to describe the observed behavior. Some connection between these traps and the constitution of the phosphor are evident but no detailed identification of the trapping levels has been attempted. The work described in this paper was carried out in 1953 and 1954. A preliminary report was presented at a symposium on impurity phenomena held at the General Electric Research Laboratories in Schenectady, New York, in 1953, and detailed reports were given at meetings of the Optical Society of America[6] and of the American Physical Society.[7] We had hoped to expand our investigation by more extensive quantitative experiments. Since this work has had to be postponed indefinitely, we feel that our results should be published despite their incompleteness.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

Most of the experiments which we shall describe have been carried out on mixed crystals of silver bromide containing about 3 mole percent of silver iodide. The crystals were made from the purest available starting precipitate. The procedure used in preparing such precipitates will be described elsewhere.[8] The molten precipitate was confined in a Pyrex ring of about 40-mm diameter, on a flat Pyrex plate. A sample disk was formed by slowly reducing the temperature in a nitrogen atmosphere. In this way, disks of acceptable optical quality were obtained, consisting of crystals of a few millimeters linear dimension. Crystals of similar composition have also been made by us, using the Bridgman[8] technique, and their optical

* Communication No. 1880 from the Kodak Research Laboratories.
[1] J. T. Randall, Trans. Faraday Soc. **35**, 2 (1939).
[2] W. Meidinger, Physik. Z. **40**, 517 (1939).
[3] W. Meidinger, Physik. Z. **41**, 277 (1940).
[4] G. C. Farnell and P. C. Burton, *Fundamental Mechanisms of Photographic Sensitivity* (Butterworths Scientific Publications Ltd., London, 1951), pp. 61–73.

[5] This conclusion has been reached independently by Dorfner in studying the luminescence of $AgBr-Ag_2S$. See Karl R. von Dorfner, Ann. Physik **16**, 331 (1955).
[6] F. Urbach and F. Moser, J. Opt. Soc. Am. **44**, 345(A) (1954).
[7] F. Moser and F. Urbach, Phys. Rev. **98**, 1557(A) (1955).
[8] Nail, Moser, Goddard, and Urbach, Rev. Sci. Instr. (to be published).

absorption spectrum has been reported.[9] These crystals show much the same luminescent properties as the polycrystalline disks.

Generally, the crystals were mounted inside a clear Dewar vessel filled with liquid nitrogen. With suitable insulation, the evaporation rate of the liquid nitrogen could be kept to a very low level. Excitation was achieved with a General Electric A100-H4 100-watt mercury lamp, in combination with a high-aperture optical system designed to excite the area of exposed crystal uniformly. The 365-mμ Hg line was the excitation generally used. This line was isolated by means of Corning Filters No. 7380 and No. 5860. Calibrated neutral densities were used to modify the incident intensity.

A high-aperture optical system was used to collect the fluorescent emission and image it on the face of an end-on Type 931A photomultiplier tube. The exciting and collecting optical systems were on the same side of the sample, both beams having about a 30° angle of incidence on the sample under study. Appropriate filters were used to keep any exciting light or infrared radiation from reaching the photomultiplier, and stray luminescence from filters, containers, etc., was carefully eliminated. The photomultiplier current was amplified and measured with a sensitive galvanometer. The galvanometer period of several seconds made it impossible to determine accurately the rapid buildup and decay of the fluorescence. A 500-watt tungsten lamp in conjunction with a quartz monochromator was used as the source of defined infrared radiation. No determination of the exciting intensity or emission in absolute units has been made.

3. RESULTS AND DISCUSSION

3.1. Volume Luminescence of Silver Bromide—Silver Iodide

Most observations on the low-temperature luminescence of silver bromoiodide, reported in the literature, have been made on photographic emulsion grains, fine powders, or polycrystalline materials. This raises the possibility that the luminescence is primarily a surface or near-surface effect.

In order to decide this question, a qualitative experiment was made on a large (2×2×1 cm), well-polished bromoiodide crystal. The crystal was slowly cooled to 77°K, and a narrow bundle of monochromatic light was allowed to enter the crystal parallel to one surface, through which the luminescence and its dependence on the exciting wavelength were observed.

At wavelengths shorter than 460 mμ, the luminescence appeared entirely confined to the entrance surface. At a wavelength of about 480 mμ, the luminescence extended distinctly about a millimeter into the crystal. Upon reaching 495 mμ, the entire 2-cm path appeared nearly uniformly luminescent. At

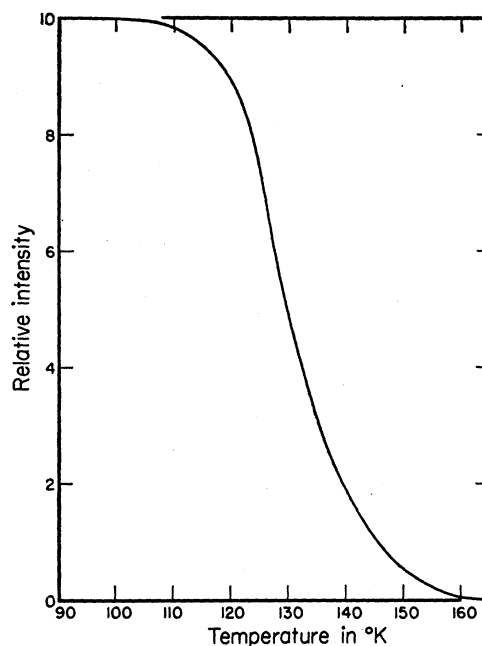[9] F. Moser and F. Urbach, Phys. Rev. **102**, 1519 (1956).

Fig. 1. Variation of fluorescence intensity with temperature in a AgBr-4 mole percent AgI emulsion.

longer wavelengths, the uniformity was maintained, but the brightness of the luminescence decreased rapidly. Measurements of the optical absorption of a similar crystal at liquid-nitrogen temperature show that at 460 mμ, the $1/e$ depth is considerably less than 0.1 mm, at 480 mμ it is about 1 mm, and at 495 mμ it is about 3 cm; beyond this wavelength the absorption decreases rapidly. The experiment appears to be a convincing demonstration that the luminescence of the silver bromoiodide is a volume effect, at least in a macroscopic sense.

3.2. Stationary Luminescence and Its Buildup

Farnell and Burton have shown[4] that the luminescent efficiency of silver bromide, containing a few percent of silver iodide, drops rapidly with increasing temperature and is negligibly small at 160°K. Figure 1, taken from the work of Farnell and Burton,[4] shows the temperature-dependence of this fluorescence.

This temperature-dependence curve became particularly interesting when Biltz[10] observed, in 1950, that the photographic sensitivity of silver bromoiodide emulsions drops rapidly at low temperatures and that this happens in the same temperature range in which the fluorescence efficiency increases. This suggested some kind of complementary relation between fluorescence and latent-image formation. At any fixed temperature in this critical range, Biltz found that the photographic efficiency decreases strongly with increasing intensity ("high-intensity reciprocity failure"),
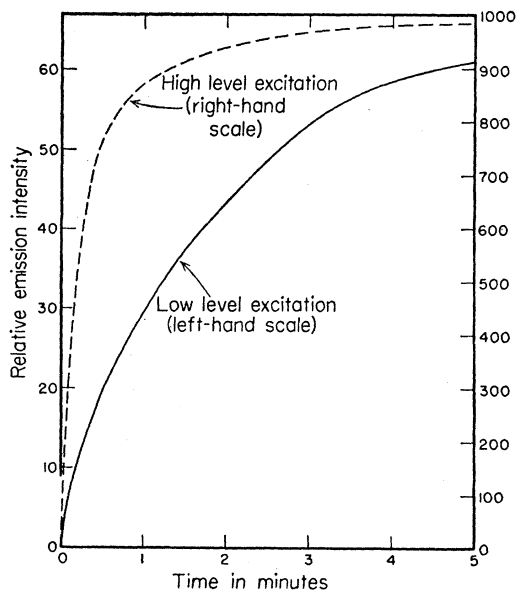
[10] M. Biltz (private communication).

FIG. 2. Relative emission intensity as a function of time of excitation for two excitation levels, in a AgBr-3 mole percent AgI crystal.

The complementary relation just mentioned would lead one to expect that the luminescence efficiency would increase with intensity. In other words, the brightness of luminescence should increase more than proportionally with the exciting intensity.

A preliminary check of the intensity-dependence of the fluorescence of a bromoiodide emulsion, carried out by Biltz and one of us, confirmed this expectation of luminescence which increases more rapidly than proportionally with the exciting intensity. Such a behavior of the luminescence was first discovered by Riehl,[11] and was studied in various aspects by others.[12-18] These studies have shown that this phenomenon is intimately connected with the occurrence of efficient trapping processes. The most conspicuous effect of trapping on luminescence, a strong afterglow, is not observed in pure silver bromoiodide crystals. The existence of efficient trapping processes, however, manifests itself clearly in the behavior of the buildup of emission under constant excitation. This growth of the luminescence has been examined on silver bromo-iodide crystals at various intensity levels. Figure 2 shows buildup curves at two different levels of exci-

tation intensity, in crystals that have had no previous exposure to actinic light. It is seen that the luminescence takes many minutes at low excitation levels to approach a stationary value.

It is convenient to discuss this phenomenon with the aid of the usual band picture of an insulating crystal (see Fig. 3), including discrete trapping levels for both electrons and holes.[19]

For this discussion, we assume that excitation corresponds to the creation of free electrons and holes, and that the green emission observed takes place by the recombination of free electrons and trapped holes at A (Fig. 3). In an unexposed crystal, at the beginning of excitation, the traps will be empty. In the initial phase of excitation, most of the freed electrons and holes will be trapped, and little recombination (and therefore little emission) will occur. Upon continued excitation, however, both electron and hole traps are gradually filled, and free electrons will, with increasing probability, recombine and emit until a stationary value of
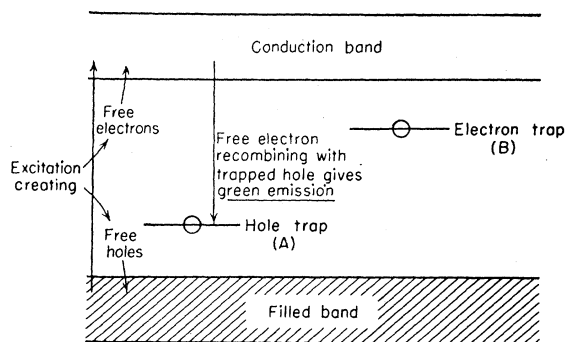

FIG. 3. Energy band model of an insulating crystal, with discrete trapping levels for electrons and holes.

emission brightness is obtained. Such a picture explains the slow buildup shown in Fig. 2.

The lifetime of the trapped states may be tested experimentally by studying the modification in the buildup curve as the result of some pre-excitation of the crystal. Figure 4 shows the initial buildup curve of an unexposed crystal. At the indicated point, the

[11] N. F. Riehl, Z. tech. Phys. 20, 152 (1939).
[12] H. A. Klasens, Nature 158, 306 (1946).
[13] Klasens, Ramsden, and Chow, J. Opt. Soc. Am. 38, 60 (1948); 38, 649 (1948).
[14] M. E. Wise and H. A. Klasens, J. Opt. Soc. Am. 38, 226 (1948).
[15] Urbach, Urbach, and Schwartz, J. Opt. Soc. Am. 37, 122 (1947).
[16] S. Roberts and F. O. Williams, J. Opt. Soc. Am. 40, 516 (1950).
[17] M. Schoen, Z. Naturforsch. 6a, 251 (1951).
[18] C. A. Duboc, Brit. J. Appl. Phys., Suppl. No. 4, S107–S111 (1954).

[19] We prefer this description of the imperfect crystal to the picture used by A. Rose [Phys. Rev. 97, 322 (1955)], who emphasizes the existence of a nearly continuous, more or less uniform, distribution of trapping levels. For photoconductance where the emphasis is on the free carriers and where the discrete levels remain, for many purposes, more or less anonymous re-combination centers, Rose's point of view appears very natural. For luminescence, where the recombination centers are more or less directly observed in the emission spectrum and in the kinetics of various emission bands, the more conventional description emphasizing a few well-defined imperfection levels is often more useful (particularly with respect to the relation of the discrete levels to the impurity content and the conditions of preparation of the crystal). If some spread in these levels is permitted and if, in Rose's model, strong peaks are admitted in the level-distri-bution, the two pictures become identical. Their relation will be treated in detail in a forthcoming paper by C. A. Duboc, of these Laboratories.

ultraviolet excitation was interrupted for a short time, and the excitation then resumed. With the second excitation, the maximum brightness is approached very rapidly, showing that most of the traps have remained filled. By increasing the interval between the initial excitation and the re-excitation, an estimate of the trap lifetime can be obtained. Figure 5 shows a set of buildup curves obtained with increasing time intervals between the first and the second excitation. For convenience of presentation, the curves have all been shifted to start at zero time. After 1 minute, some of the acceleration caused by pre-excitation is lost, but, even after a pause of 2 hours, the buildup rate is still appreciably faster than that of the unexposed sample, indicating that many traps are still filled.

No afterglow of more than a fraction of a second's duration has been observed in these crystals. This indicates that only a very small fraction of the electrons

FIG. 5. Relative emission intensity as a function of time of excitation for varying dark periods since the previous excitation. Data are taken on a AgBr-3 mole percent AgI crystal.
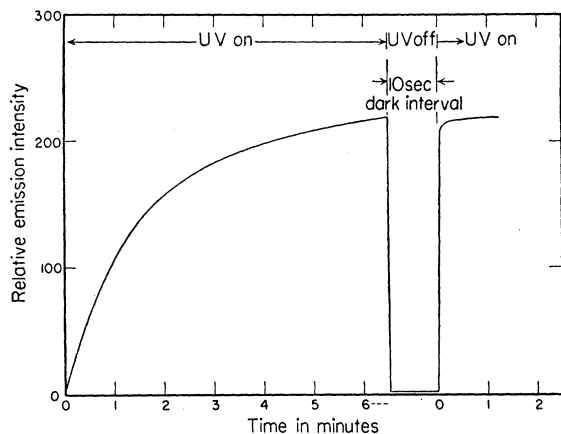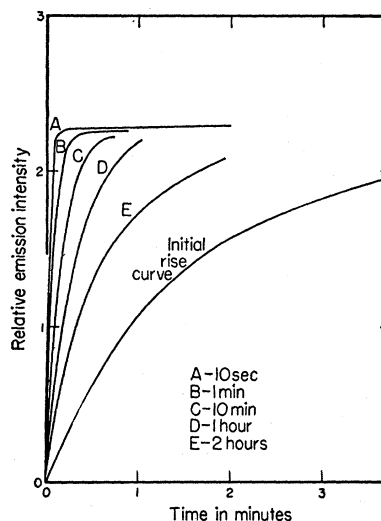

FIG. 4. Relative emission intensity as a function of time of excitation for both an initial excitation and re-excitation after a short dark period. Data are taken on a AgBr-3 mole percent AgI crystal.

rence in two-center models. For the model proposed here, this analysis shows that the assumption of a negligible probability for the release of the trapped electrons into the conduction band has a definite and testable consequence: it requires that the fluorescent emission intensity increase with the 1.5th power of the exciting intensity over an appreciable intensity range (see Appendix). Thus, the model which serves to explain the general features of the observed luminescence predicts a specific dependence of emission intensity on excitation intensity. Measurements carried out on a silver bromoiodide crystal at 77°K with excitation by 365-mμ radiation are shown in Fig. 7. Brightness and excitation intensity are plotted here on logarithmic scales. It is seen that over a range of 3 powers of ten of exciting intensity, the brightness increases with the 1.5th power of this intensity. Since the 365-mμ radiation is strongly absorbed in the crystal, this nonlinear dependence must actually extend over an even larger range.

trapped at the end of excitation return to the ground state via the conduction band, since this would be accompanied by a distinct afterglow of the same color as that of the fluorescence. Therefore, most of the recombination must take place by release of trapped holes into the valence band and subsequent recombination with trapped electrons, this recombination occurring without visible emission. In other words, the absence of a visible afterglow means that the thermal release of the electrons from their traps into the conduction band has a very small probability. Figure 6 shows the band model of Fig. 4, omitting, however, the transition just mentioned, and identifying the radiative and non-radiative recombinations. Models very similar to these have been proposed previously in the discussion of non-linear zinc sulfide phosphors. More recently, Duboc[18] has carried out a comprehensive analysis of the types of nonlinear behavior and the generality of their occur-
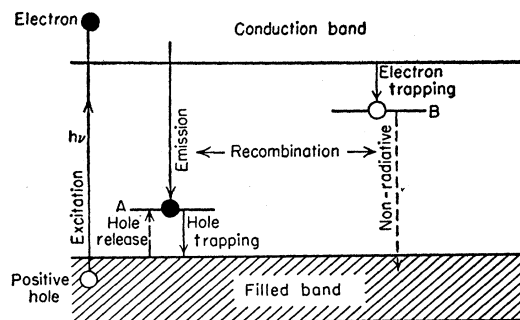

FIG. 6. Energy band model of silver halide phosphor. Note the deliberate omission of the transition corresponding to thermal release of electrons into the conduction band.
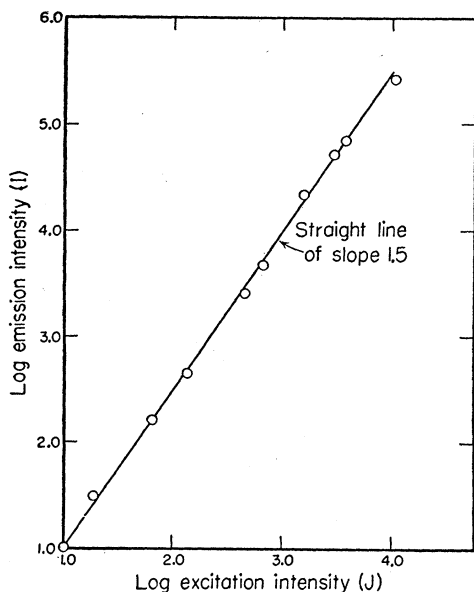
Fig. 7. Relative emission intensity as a function of excitation
intensity for a AgBr-3 mole percent AgI crystal

3.3. Quenching by Infrared Radiation

Irradiation of silver bromoiodide crystals with near-
infrared shortly after the termination of excitation
reveals a weak and short stimulation effect. This
stimulability, however, vanishes nearly entirely within
1 minute after excitation, and is probably not related
to the large majority of filled traps.

If, however, the sample is irradiated with infrared
during excitation, a very strong quenching effect is
observed. Figure 8 shows a typical curve obtained by
first letting the crystal approach an equilibrium emission
intensity under constant ultraviolet excitation, and
then adding infrared radiation. A short burst of stimu-
lation is observed, followed by the fairly rapid establish-
ment of a much lower stationary brightness level. This
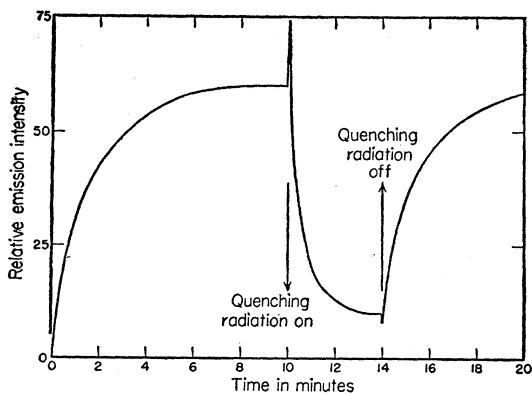quenching of the fluorescence occurs over a large

Fig. 8. Simultaneous quenching effect in AgBr-3 mole percent
AgI crystal. The emission intensity is plotted as a function of time.
The exciting radiation is on at all times; the quenching radiation is
turned on after 10 minutes and off after 14 minutes.

spectral range, with radiation near 0.8 μ being the most
effective.

The effect of infrared radiation on the fluorescence
also manifests itself in its effect on the behavior of the
buildup curves. Figure 9 shows the effect on the buildup
curve of infrared radiation applied in the interval
between the two excitations. The figure shows first an
initial buildup curve on a previously unexposed crystal,
then the subsequent accelerated rate after a 1-minute
dark interval. After attaining the stationary level, the
excitation is again terminated, but the sample is now
irradiated with infrared. The subsequent third buildup
curve now has the low-rate characteristic of an un-
exposed crystal: the acceleration of the buildup rate by
pre-excitation has been almost totally destroyed.

These observations on the effects of long-wavelength
radiation may again be simply interpreted on the basis
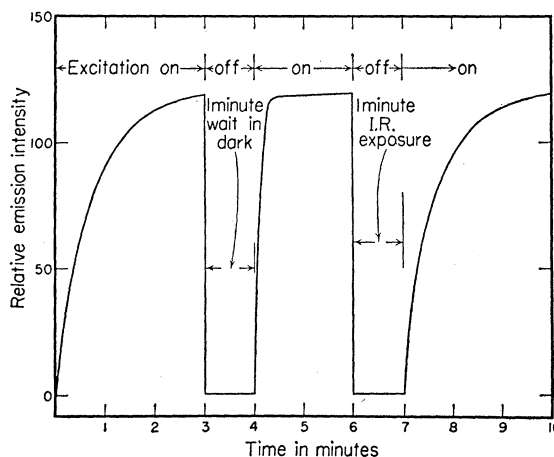of the model given in Fig. 6. The long-wavelength

Fig. 9. Effect of prior infrared radiation on the buildup of
emission under constant excitation, in a AgBr-3 mole percent
AgI crystal.

absorption may be attributed to a hole release at the
hole trap (A). This process increases the probability of
radiationless recombination of free holes with trapped
electrons, and at the same time tends to block the
radiative electron capture at A. Such a mechanism
accounts qualitatively for the observed simultaneous
quenching as well as for the loss of acceleration of
buildup by previous exposure. The model used here is
of the type usually employed to represent phosphors
with a low concentration of luminescent centers.
In the present case, it appears certain that at least one
of the levels, A and B (most probably A), is produced
by the presence of iodide ions (probably in some special
arrangement; perhaps an iodide ion next to a silver
vacancy).

3.4. Impurity-Activated Crystals

The general study of phosphorescence has gained
much by the observation of stimulation and quenching

in sulfide phosphors containing two kinds of activating centers, each with an observable emission band. Something similar can also be achieved in the silver halide phosphors. In order to do so, one must introduce a second activating center with visible emission. This can be done on the basis of observations made on simple silver bromide and silver chloride crystals.

We have found that it is possible to produce impurity-activated phosphors with the silver halide as a matrix, with impurity concentrations of the same order of magnitude as those used in sulfide phosphors.[20] Silver bromide, for example, which is nonluminescent at 77°K, shows a strong orange-red luminescence if $CdBr_2$ or $SrBr_2$ is introduced into the melt in concentrations from 10^{-6} to 10^{-3}.[21] A very similar activation by strontium is obtained if it is added to silver bromo-iodide. Upon ultraviolet excitation, the green (iodide) luminescence and the red (strontium) luminescence can be observed simultaneously.

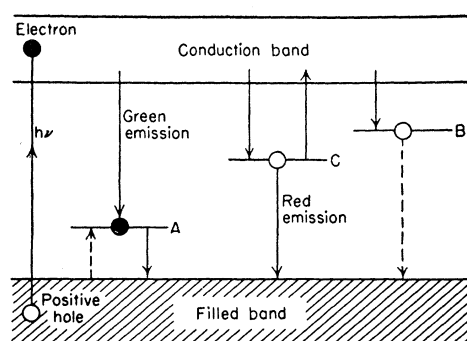If the luminescence of these strontium-activated

FIG. 10. Energy band model of silver halide phosphor with an activator. The C-center is associated with the introduction of strontium into the AgBr-3 mole percent AgI phosphor.

bromoiodide crystals is observed after excitation, there appears, in addition to the red strontium emission, a quite distinct green iodide emission, which was almost entirely missing in the pure bromoiodide (see Sec. 3.2). This strongly suggests that strontium introduces centers which are capable of effectively trapping electrons, but which, unlike the electron traps attributed to the iodide, release them at an appreciable rate into the conduction band, where they become available for the green emission. Incorporating such a center into our previous model leads to the model shown in Fig. 10. The centers introduced by strontium are labeled C. If the same strontium centers are responsible for the red emission, this emission must be assigned to the recombination of the trapped electrons with free holes, the transition corresponding to the radiationless

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[20] A different result stated by Farnell and Burton[4] does not really contradict our findings; these authors apparently did not investigate the activators which we found most effective.

[21] Other examples: a red emission is produced in AgCl by additions of Ba and Ca; an infrared emission is produced by monovalent copper.

transition in the B centers. We have been led to this scheme by trying to represent, in the simplest possible way, the changes which the introduction of strontium causes in the fluorescence color and in the afterglow of the bromoiodide. This model has, however, several definite consequences which could be tested by experiment. (1) The presence of electron release into the conduction band weakens, in this model, the reason for occurrence of the nonlinearity of the green emission. Thus, its intensity-dependence should become weaker than the observed 1.5th power. (2) The same electron release, if caused by absorption of radiation, should produce a stimulated emission of the green band. (3) The release of holes at the A centers, which produced radiation-quenching in the strontium-free phosphor, should now increase the probability of the radiative transition of the C centers, that is, it should stimulate the strontium emission. (4) The same absorption process which produces the stimulation of the green emission should reduce the probability of the red emission, i.e., cause a simultaneous quenching effect of the latter. (This effect would be entirely analogous to the simultaneous quenching of the green emission in the strontium-free crystals.) A series of careful visual observations on the strontium-containing crystals showed that the various phenomena predicted by the model actually occur. Crude qualitative observations on the spectral distribution of the effect of the quenching and stimulating radiations were at least compatible with the predictions.

While the picture given here yields a simple description for a large variety of qualitative observations, no attempt has been made to subject it to any quantitative test. It can, however, serve as a guide for further investigation. Whatever the model, our results seem to establish that the silver halide phosphors belong to the large class of photoconducting phosphors capable of activation by small amounts of impurities, in which the trapping of electrons and holes, their release and migration, and their recombination determine the luminescence effects.

3.5. Fatigue Effects

While the general character of the silver halides as photoconducting phosphors appears established, some effects have been observed which seem to distinguish the silver halides. Like many other phosphors, the silver bromoiodide crystals show a gradual decrease of luminescent efficiency if excitation at high-intensity levels is continued for long periods of time. The remarkable feature of the "fatigue" of silver bromoiodide is that the decrease of efficiency is greater if the luminescence is *observed* at low-intensity levels. If, for example, one half of a silver bromoiodide sample is exposed to strong ultraviolet irradiation at the temperature of liquid nitrogen for some length of time, and the fluorescence is then observed at this low tempera-

ture, the irradiated half appears darker than the un-exposed half, *if* the observation is made using low ultraviolet intensity. If high intensity is used, the two halves become practically indistinguishable. The exposure involved does not produce any visible darkening of the silver halide, and the effect cannot be ascribed to any shielding effect due to a printout process occurring at this low temperature.

Although we have no clear interpretation of this effect, we feel that processes other than purely electronic ones play a role. It appears likely that strong exposure produces some changes of the luminescence centers which involve ionic motion over small distances in the crystal. This might be the first phase of the process which, in its later stages, may lead to the separation of silver in the crystals.

ACKNOWLEDGMENTS

The authors are indebted to several members of these Laboratories for their cooperation: to C. A. Duboc for valuable discussions of the theoretical model, to P. E. Goddard for the materials used, and to N. R. Nail for his assistance with experimental techniques.

APPENDIX

Let the concentrations of the centers A and B be L and P, respectively, the concentrations of free electrons and holes, n and p. The electron- and hole-capturing processes are characterized by four rate constants σ_1, σ_2, σ_3, and σ_4, and the hole and electron release by constants k and κ. Furthermore, let the fraction of P with trapped electrons be x and the fraction of L with trapped holes be y. At sufficiently low intensities, the model of Fig. 4 is then described in its steady state by the following set of equations (which are obtained from Eqs. (2), (13), and (17) in Duboc's paper[18] if κ is made zero and if n and p are low enough):

$$xP = p + yL,$$

$$ky = p\sigma_4,$$

$$xp\sigma_3 = n\sigma_1.$$

The intensities of excitation and emission are given by

$$J = p\sigma_3 xP,$$

$$I = n\sigma_2 yL.$$

Solving for I, one obtains

$$I = J^{\frac{3}{2}} \frac{\sigma_2 L}{\sigma_1 P} \frac{\sigma_4}{[k\sigma_3(k+\sigma_4 L)]^{\frac{1}{2}}}.$$

Thus, the intensity-dependence discussed in the text appears to be valid at all sufficiently low intensities of excitation.

If the rate of electron release is not exactly zero, the proportionality of I with the 1.5th power of J will still occur over a finite range of intensities, provided that κ is sufficiently small. More precisely, it is required that κ fulfills the following set of conditions:

$$\kappa \ll k\sigma_3 P/(k+\sigma_4 L),$$

$$\kappa \ll k\sigma_3/\sigma_4,$$

$$\kappa \ll k\left[\frac{\sigma_1\sigma_3 P}{\sigma_2(k+\sigma_4 L)}\right]^{\frac{1}{2}},$$

$$\kappa \ll \sigma_1 P,$$

$$\kappa \ll k\sigma_1\sigma_3 P/(\sigma_2\sigma_4 L).$$

If these conditions are met, the intensity-dependence will be linear at very low intensities, a transition to the power $\frac{3}{2}$ taking place near

$$J = \frac{\kappa^2}{\sigma_3}\left(\frac{k+\sigma_4 L}{k}\right).$$

What happens at high intensities depends on the exact relation between the parameters. Our observations indicate that, at high intensities, a second linear region with an efficiency close to 1.0 is obtained. A more detailed analysis shows that this could be expected if the last of the five conditions for κ is the most stringent one, and the square of the ratio between the right and left side of this inequality determines the range of J over which the power $\frac{3}{2}$ is valid.